

CONNECTING PIECES FOR CARBON MATERIAL ELECTRODES

5 Background of the Invention:

Field of the Invention:

The invention relates to connecting pieces for carbon material electrodes. In particular, the invention relates to connecting pieces that are produced by mixing cokes, pitches, and carbon
10 fibers to provide a mass, and by shaping the material mass. The shaped pieces are used for connecting carbon material electrodes, in particular graphite electrodes.

Carbon material electrodes, in particular graphite electrodes,
15 are used in electric arc furnaces in the steel industry. The electrodes consist of individual cylindrical elements connected to one another, further elements being added in each case depending on the firing. The electrodes are usually connected to one another mechanically and in an electrically
20 conductive manner by connecting pieces (also referred to as connecting pins, connecting nipples, and electrode nipples). Here, the connecting pieces have the shape of a double cone (two truncated pyramids joined to one another at the base) having threads on the lateral surfaces, which fit into
25 corresponding recesses of the cylindrical electrodes, which recesses are formed centrally in the end faces.

Owing to the thermal load, it is necessary to adapt the thermal expansion of the connecting pieces and of the electrodes to one another in such a way as to prevent the formation of stresses which may lead to fracture or other damage at the connecting point. In the past, connecting pieces reinforced with carbon fibers have been proposed. For example, U.S. Patent No. 4,998,709 describes graphite connecting pieces that are reinforced by carbon fibers which are obtained from mesophase pitch and are present in a proportion by mass of from 8 to 20% in the molding material used for the production. International PCT publication WO 01/62667 describes a similar process, but the fibers likewise obtained from mesophase pitch have a lower modulus of elasticity and are used in a smaller proportion by mass (from 0.5 to 5% in the molding material). This process leads to a reduction in the coefficient of thermal expansion in the direction of extrusion and of the main axis of the connecting piece.

The stresses usually occurring in fiber-reinforced materials are due to the different coefficients of thermal expansion of fibers and matrix. Carbon fibers are practically dimensionally stable in the fiber direction (i.e. the coefficient of thermal expansion is small and negative), whereas, for example, in the case of glassy carbon this coefficient is of the order of magnitude of $3 \cdot 10^{-6} \cdot K^{-1}$.

In the investigations on which the present invention is based, it has been found that further improvement compared with the above-mentioned prior art processes (US 4,998,709 and WO

5 01/62667) can be achieved if carbon fibers whose surface has been treated before mixing into the molding material and has been provided with a polymer coating are used in the molding material for the production of the connecting pieces.

Connecting pieces according to the invention have a reduced
10 longitudinal (i.e., in the direction of the axis of the cylindrical electrode and of the connecting piece) coefficient of thermal expansion and increased strength. Owing to these properties, the connecting pieces according to the invention withstand not only the carbonization temperatures below 1000°C
15 but also a subsequent graphitizing treatment at above 3000°C.

It has become known in the art that carbon fibers can be anodically oxidized in an electrolyte solution (J.B. Donnet and R.C. Bansal, *Carbon Fibers*, Marcel Dekker Inc. New York
20 (1990)). In that surface treatment, oxygen-containing groups form on the fiber surface, as a rule strongly or weakly acidic carboxyl groups and hydroxyl groups, C-H groups activated by carbonyl groups (C-H acidic groups), and basic pyrone-like surface groups (H.P. Boehm, E. Diehl, W. Heck, R. Sappok,
25 Angew. Chem. 76 (1964), 742; B.R. Puri, in Walker: Chemistry

and Physics of Carbon, Vol. 6, Marcel Dekker, New York (1971), 191).

Oxygen groups can be produced on the fiber surface also by
5 thermal oxidation without the necessity of subsequent washing
out for removing electrolytes. Oxygen in various
concentrations, oxygen-halogen mixtures, ozone, carbon dioxide
or oxides of nitrogen are described as an oxidation medium. A
detailed discussion of these topics is found in J. Cziollek
10 ("Studien zur Beeinflussung des Verstärkungsverhaltens von
Kohlenstofffasern durch Oberflächenbehandlung der Fasern und
durch Verwendung eines Kohlenstoff/Kohlenstoff-Skelettes als
Verstärkungskomponente" [Studies on influencing the
reinforcing behavior of carbon fibers by surface treatment of
15 the fibers and by the use of a carbon/carbon skeleton as a
reinforcing component], Thesis, University of Karlsruhe
(1983), p. 40 et seq.).

In the case of carbon fiber-reinforced carbon ("CFC"), reduced
20 reactivity of the fiber surface is regarded as a basic
requirement for good utilization of the fiber properties. The
reduced reactivity is intended to enable the matrix to shrink
away from the fiber surface. The shrinkage cracks are then
filled by repeated reimpregnation/recarbonization steps
25 (impregnation, for example, with pitches and combustion in the
absence of oxidizing agents). Consequently, carbon bonding

bridges between fiber surface and matrix are produced (J. Cziollek, op. cit.). The restoration of the weakened fiber/matrix adhesion brought about by newly created surface groups as a result of the reimpregnation step has also been
5 discussed (K.H. Giegl: "Studien zur Oberflächenchemie von Kohlenstofffasern und zur Entwicklung von Kohlenstoff-Hohlfasern" [Studies of the surface chemistry of carbon fibers and of the development of hollow carbon fibers], Thesis, University of Karlsruhe (1979)).

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In contrast with these experimental findings in the case of CFC composites, an oxidative surface treatment of the fibers in the present invention has surprisingly proved to be advantageous for the properties of a composite produced
15 therewith.

The present invention therefore relates to connecting pieces for carbon material electrodes, the connecting pieces containing carbon fibers whose surface has been oxidatively
20 activated and which additionally have a carbonized coating. The surface coating is the carbonization product of a coating material (sizing) selected from wax, pitch, natural resins, thermoplastic and thermosetting polymers.

The invention furthermore relates to a process for the production of connecting pieces that contain the fibers treated according to the invention.

5 With the foregoing and other objects in view there is provided, in accordance with the invention, a connecting piece for carbon material electrodes. The connecting piece includes carbon fibers having oxidatively activated surfaces, and an added carbonized coating. The carbonized coating is a
10 carbonization product of a coating material selected from the group consisting of wax, pitch, natural resins, thermoplastic polymers, and thermosetting polymers.

In the process according to the invention, the surface of the
15 carbon fibers is activated by oxidation in a first step, the fibers are then provided, in a second step, with a surface coating comprising a coating material selected from wax, pitch, natural resins or thermoplastic or thermosetting polymers, the coated fibers are optionally treated in a third
20 step at a temperature of from 750 to 1300°C for carbonization of the coating, are mixed in a fourth step with coke having a mean particle size in the range from 0.05 to 4 mm, pitch having a softening temperature in the range from 70°C to 150°C and optionally further additives and shaped to give
25 cylindrical bodies, the cylindrical moldings are carbonized and then graphitized in a fifth step, and the graphitized

moldings are turned, in a sixth step, to give the connecting pieces having threads.

It is preferable to use carbon fibers in the form of fiber tow
5 comprising from 1000 to 60,000 individual filaments, which, after the third process step, are cut to give short fibers having an average length of from 0.5 to 40 mm.

It is furthermore preferable to use carbon fibers in the form
10 of heavy tow comprising from 40,000 to 2,000,000 individual filaments, which, after the third process step, are cut to give short fibers having an average length of from 0.5 to 40 mm.

15 It is furthermore preferable if the activated carbon fibers are coated, in the second step, in an aqueous or solvent-containing bath containing a dispersion or solution of a coating material selected from wax, pitch, natural resins or thermoplastic or thermosetting polymers.

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It is furthermore preferable if the coated carbon fibers are treated, in the third step, at a temperature of from 900 to 1200°C for carbonization of the coating.

It is furthermore preferable if, in the fourth step, a mixture containing for each 100 kg of coke, from 10 to 40 kg of a pitch and from 0.2 to 20 kg of carbon fibers is prepared.

- 5 It is furthermore preferable to add, as further additive, from 0.1 to 1 kg of an iron oxide pigment having a mean particle size of from 0.1 to 2 μm .

The surface coating is effected in particular using polymers
10 which have a sufficient carbon yield at carbonization temperatures of, preferably, from about 750 to about 1300°C. Polyurethane resins, phenol resins and pitches having a C residue of at least 40% of the mass of the coating material used are particularly suitable.

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The carbonization of the coating material can be effected in a thermal treatment step prior to mixing into the molding material, or preferably simultaneously with the combustion after green production.

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Carbon fibers which are obtainable by carbonization of oxidatively stabilized polyacrylonitrile fibers in a known manner are preferably used. A thermal treatment of the fibers in the range from 1500°C to the graphitizing temperature
25 (1800°C to about 3000°C, in some cases also above 3000°C)

prior to mixing in can be dispensed with. The modulus of elasticity of the fibers is preferably from 200 to 250 GPa.

The surface activation of the carbon fibers is effected by
5 oxidation in an aqueous bath or by an oxygen-enriched gas stream at a temperature of from 400 to 600°C, the gas stream also serving for fanning out the fiber tow. In a preferred manner, it is also possible to oxidize the carbon fibers electrochemically, i.e. anodically in aqueous baths.

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Aqueous solutions of salts of oxidizing acids, such as nitrates, sulphates, chlorates, bromates and iodates, and the stated acids themselves are suitable as the oxidation bath; solutions which contain volatile oxidizing agents are
15 preferred, the reduction products of these oxidizing agents preferably likewise being volatile. Here, substances which are defined as being volatile are those which are removed completely or substantially completely (with an evaporation residue which is not more than 0.5% of the mass of the treated
20 fibers) on drying the treated fibers, for example in an air stream or on godets. Particularly preferred oxidizing agents are oxidizing acids, such as nitric acid, chloric acid or mixtures of these with neutral or salt-like inorganic oxidizing agents, such as hydrogen peroxide, chromates,
25 permanganates and hypochlorites ($\text{KMnO}_4/\text{H}_2\text{SO}_4$, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, $\text{HOCl}/\text{H}_2\text{O}/\text{NaOCl}$). Mixtures of nonoxidizing acids with salt-like

oxidizing agents are also suitable, for example the mixtures of hydrochloric acid and chlorates, known as euchlorine. In an electrochemical (anodic) oxidation, it is sufficient to establish adequate conductivity by dissolving acids, bases or
5 salts in water.

After an electrochemical treatment (anodic oxidation) and with the use of oxidizing solutions (in particular salt solutions), it is necessary to wash the fiber tow with demineralized
10 water, preferably at least two baths being arranged in series. The acid-treated fibers may also be washed, it being possible to omit the drying step.

The carbon fibers activated in this manner with oxygen-
15 containing groups are then provided with the abovementioned surface coating, the dried or only washed fibers being passed through an aqueous impregnating bath, the excess solution containing coating materials being squeezed out in a known manner, and the fiber tow being dried, for example on heated
20 godets.

The impregnating bath is preferably an aqueous formulation of said coating materials, for example an aqueous dispersion of waxes, in particular polyolefin waxes based on polyethylene or
25 polypropylene, and montan waxes, or waxes synthesized by esterification of fatty alcohols with long-chain fatty acids

having 12 to 40 carbon atoms. Furthermore, it is possible to use dispersions of polyurethane resins, of activated polyolefins (activated, for example, by grafting with maleic anhydride) or the copolymers thereof (for example with vinyl alcohol or vinyl acetate) or of phenol resins. It is also possible to treat the activated carbon fibers with organic compounds, in particular those based on pitches, dissolved in organic solvents. Pure pitches in a suitable low-viscosity form may also be used for the coating.

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The concentrations of the coating formulations are usually such that a solids mass fraction of from 0.5 to 30%, originating from the coating, results on the fiber surface. A range of from 3 to 15% is preferred. This results in a mass fraction of, preferably, from 0.2 to 15% of the carbonized coating on the fibers.

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Carbon fibers based on (carbonized) polyacrylonitrile are preferably used, since it has been found that these undergo the least damage by the mixing and shaping process on mixing to give the molding materials according to the invention. Their modulus of elasticity is as a rule not as high as that of carbon fibers based on mesophase pitch. This means lower rigidity and therefore also less sensitivity to shearing. Both the additionally applied coating and the conversion of this

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coating into a carbon layer lead to additional mechanical protection.

It was observed that the comminution of the fibers on mixing
5 in is substantially reduced compared with the HM fibers (high-modulus fibers) sensitive to shearing. The degree of utilization of the amount of fibers used is thus higher, leading to a further cost benefit in addition to the lower costs of the HT fibers (high-tenacity fibers).

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The meterability of the fiber bundle cut into short fibers (preferably having an average length of from 0.5 to 40 mm) is also improved by the sizing applied. Uncoated individual filaments having lengths of more than 2 mm tend to agglomerate
15 and therefore cannot be metered in a controllable manner.

The fiber tows used preferably have from 1000 to 60,000 individual filaments, and multifilament tows based on heavy tow having more than 40,000 filaments and up to 2,000,000
20 filaments are also preferred.

It is also possible for the carbon fibers to be present in the form of parallel filaments (so-called "UD tapes"), woven fabrics, warp-knitted fabrics, knitted fabrics and/or nonwoven
25 fabrics.

The connecting pieces according to the invention preferably have a linear coefficient of thermal expansion in the extrusion direction of from -0.5 to $+0.1 \mu\text{m}/(\text{K}\cdot\text{m})$. The extrusion direction is the direction parallel to the lateral surface of the generally cylindrically shaped blanks which, after the carbonization and combustion, are processed by turning or milling and into which the required threads are cut. Perpendicular to the extrusion direction, the linear coefficient of thermal expansion is preferably from 1.7 to $2.1 \mu\text{m}/(\text{K}\cdot\text{m})$.

The mass fraction of carbon fibers in the connecting pieces is preferably from 0.2 to 10% .

It was surprisingly found that connecting pieces which were produced using such carbon fibers not only are distinguished by the desired low values for the coefficients of thermal expansion but also have increased strength. Both are indicative of good fiber-matrix adhesion. This can be shown, for example, by preparing an electron micrograph of the fracture surface of connecting pieces destroyed in a tensile test or in a bending test and comparing this with a fracture surface of connecting pieces which contain fibers without such a treatment.

These findings are illustrated by the appended micro-
photographs. The construction and method of the invention,
together with additional objects and advantages thereof will
be best understood from the following description of specific
5 examples when read in connection with the accompanying
drawings.

Brief Description of the Drawings:

Fig. 1 is a micrograph, taken by an electron microscope, of a
10 fracture surface of a connecting piece (connecting pin) in
which carbon fibers according to the invention were used; and

Fig. 2 is a similar electron micrograph of a fracture surface
of a connecting piece (connecting pin) in which carbon fibers
15 from mesophase pitch were used as reinforcement.

Description of the Preferred Embodiments:

Referring now to the figures of the drawing in detail, a
comparison of the two micrographs renders it immediately clear
20 that, in the case of fibers from mesophase pitch without the
treatment according to the invention (Fig. 2), the fibers are
simply pulled out of the matrix in the event of a fracture and
they leave behind a void, whereas, in the case of a connecting
piece comprising fibers treated according to the invention by
25 activation and coating, said fibers adhere firmly in the

matrix and are not pulled out of the matrix in the event of a fracture (Fig. 1).

In a connecting piece which is produced according to the invention, the fracture surface displays matrix cracks and cracks of the fibers in the fracture surface. However, the matrix reveals no holes from which the reinforcing fibers were pulled out on failure. The adhesion of the fibers to the matrix is evidently so great that the force required for pulling the fibers out of the matrix ("pull-out") is greater than the tensile strength of the fibers. In a comparison with a connecting piece which was produced according to the prior art using carbon fibers obtained from mesophase pitch and without the treatment according to the invention, the pull-out holes of the fibers from the fracture surface are clearly detectable.

It is furthermore surprising that, as explained above, no destruction of the fibers as a result of internal stresses occurs in spite of the presumably better binding of the fibers in the matrix due to the surface treatment.

The graphitized bodies which are produced from the materials according to the invention have the following properties:

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Density	in kg/m ³	1740 to 1850
Modulus of elasticity* in the tensile test	in GPa	20 to 25
Flexural strength*	in MPa	25 to 33
Resistivity*	in $\mu\Omega\cdot m$	3.0 to 4.5
Longitudinal* coefficient of thermal expansion	in $\mu m/(K\cdot m)$	-0.5 to 0.1
Transverse coefficient of thermal expansion	in $\mu m/(K\cdot m)$	1.7 to 2.1

* Parallel to the extrusion direction

Connecting pieces comprising these graphitized bodies lead, in
5 a practical test, to substantially reduced susceptibility to
cracking due to thermal stresses.

The invention is explained by referring to the following
examples.

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Example 1

A fiber tow (7 x 60,000 filaments having a fiber diameter of 7
 μm) comprising carbonized polyacrylonitrile fibers was
subjected to anodic oxidation. For this purpose, the fiber tow
15 was passed through a bath having an effective length of about
1 m and containing an aqueous solution of sodium hydroxide

(5 g in 100 g of the solution) at a speed of 1 m/min according to the method described in U.S. Patent No. 4,704,196, example 3. The bath was continuously circulated. A sinusoidal voltage of 5 V was applied, and the current was about 70 A.

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Thereafter, the fiber tow was washed out in a two-stage wash bath containing demineralized water and was squeezed out. The tow was then passed through a sizing bath containing 10 g of aqueous dispersed polyurethane resin in 100 g of the dispersion and having an effective length of 0.5 m, squeezed out, and dried over godets at 120°C. The fiber tow was cut to give staple fibers about 6 mm long.

Example 2

15 A molding material was prepared from:

- 100 kg of needle coke having a mean particle size of 0.5 mm;
- 26 kg of cold tar pitch having a softening temperature (SPM) of 110°C;
- 20 ▪ 3 kg of PAN-based carbonized carbon fibers having a diameter of 7 μ m and an average length of 6 mm, which were anodically oxidized and provided with a polyurethane coating according to example 1; and

- 0.5 kg of iron oxide of pigment quality (particle size range from 0.1 to 2 μm).

The material was mixed for 0.5 hour in a kneader-mixer at
 5 160°C, extruded at 120°C to give a cylindrical extrudate and,
 after cutting to a length of about 3000 mm, combusted at 800°C
 for 500 hours. The combusted cylindrical carbon bodies were
 then impregnated three times with an impregnating pitch (SPM
 80°C) and subsequently combusted at 800°C. The impregnated and
 10 subsequently combusted carbon bodies were graphitized in a
 conventional manner at about 3000°C.

The following values were measured on the cylindrical graphite
 bodies having a diameter of 305 mm and a length of 2300 mm (a
 15 corresponding mixture without the addition of fibers was
 prepared as a comparison, and the measured values for the
 graphite bodies produced therefrom are shown in brackets):

Longitudinal coefficient of thermal expansion	in $\mu\text{m}/(\text{K}\cdot\text{m})$	0.06 (0.14)
Transverse coefficient of thermal expansion	in $\mu\text{m}/(\text{K}\cdot\text{m})$	1.88 (1.88)
Flexural strength parallel to the extrusion direction	in MPa	28.5 (26.0)

Although the invention is illustrated and described herein as embodied in a connecting pieces for carbon material electrodes, it is nevertheless not intended to be limited to the details shown, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

This application claims the priority, under 35 U.S.C. § 119, of German patent application No. 103 12 370.9, filed March 20, 2003; the disclosure of the prior application is herewith incorporated by reference in its entirety.